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# Effect of ultrasonic waves on crystallization from a supersaturated solution of alum

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The effect of ultrasonic waves on the particle size and distribution of precipitated crystals from a slowly cooled supersaturated solution of ammonium aluminium sulphate hydrate was investigated. It was found that ultrasonic irradiation greatly promoted the homogeneity in particle sizes of the crystals precipitated. Average particle sizes of both the mechanical stirred and the ultrasonically treated samples did not change much if the initial solute concentration was beyond the saturation solubility of the solution. The higher acoustic intensity of the higher frequency ultrasonic transducer resulted in a larger average particle size in the recrystallization process.

## 1. Introduction

Ceramic powder preparation by liquid coprecipitation processing is usually conducted by adding a suitable reagent to a solution of the substance to be precipitated. Even when the reagent is dilute and is added slowly to the solvent, it is inevitable that the concentration of the reagent in different regions will vary locally [1]. This may cause abnormal growth of some precipitated particles and will result in a large deviation of particle size distribution. The introduction of ultrasonic waves into the solvent might possibly resolve this problem. The application of ultrasonic energy to chemical processing may be classified into two categories: (a) to yield a product superior to that obtainable by conventional means, e.g. emulsion of smaller and more uniform particle sizes, and (b) to enhance chemical reactivity in unit operations, e.g. solid–liquid precipitation. However, reports of the effects of solution concentration, ultrasonic frequencies and acoustic energy on the precipitated particles' size and distribution are generally lacking. It was the purpose of this research to study the influence of ultrasonic waves on the behaviour of particle precipitation from a solution. A better understanding could thus be derived in applying ultrasonic technology for the preparation and production of ultra-high-quality chemicals and/or ceramic powders.

## 2. Experimental procedure

### 2.1. Material

The solute material chosen in this experiment was ammonium aluminium sulphate hydrate, $(NH_4)_2$-$Al_2(SO_4)_2 \cdot 12H_2O$, or Alum. This material dissolves readily in water and has different solubilities depending on temperature. When precipitating from a solution, it does not involve any chemical reaction but simply crystallizes from the supersaturated solution in order to maintain the equilibrium state of the solution. However, under natural cooling conditions without any disturbance/stirring to the solution, precipitation of Alum crystals does not readily occur. Introduction of precipitation energy from an external source, such as mechanical stirring (MS) or ultrasonic vibration (US), greatly promotes the crystallization process (see Fig. 1). It is thus an ideal material with which to study the effects of ultrasonic vibratory waves on the sizes and distribution of the precipitated particles or crystals.

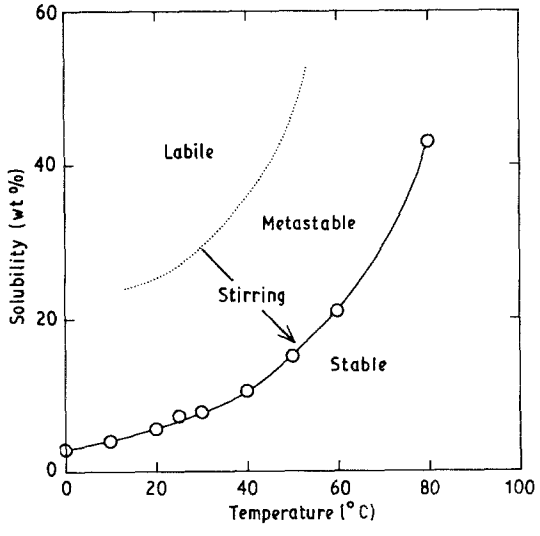


*Figure 1* (——) Solubility curve and (– – –) virtual supersaturation curve of Alum. The metastable region is reduced by stirring.

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## 2.2. Apparatus and procedures

Commercially available Alum crystals were dissolved in distilled water and heated to 60 °C. No further refinement of the material and no degassing of the solution were carried out. The concentration of the initial solution was 16.7, 23.1, and 28.6 wt %, respectively, although most of the subsequent tests were performed with 23.1 wt % Alum solution. The solution was then slowly cooled in an ultrasonic apparatus, as illustrated in Fig. 2. Three ultrasonic frequencies were employed, 200, 550 and 1740 kHz. The temperature of the solution was continuously recorded using a copper–constantant thermocouple, 0.1 mm in diameter. The temperature of the cooling system was set at 20 °C which is the temperature of the circulating water. When the temperature of the solution reached 30 °C, the recrystallized Alum particles were immediately filtered and separated from the solution, and carefully wiped dry to prevent further crystallization from residual liquid. It took about 40 min to cool the solution from 60 °C to 30 °C and the cooling history of each test varied little because the volume of the solution (60 ml) was considerably less than that of the cooling medium (3000 ml). The recorded maximum deviation in temperature was 2 °C and in cooling time was 3 min only.

## 2.3. Output power measurement

The optimum power input setting was determined for each ultrasonic transducer by observing the doming up of the liquid surface without splashing. Because the electro-mechanical coefficient of the ultrasonic transducer varies with applied voltage and frequency, it is more favourable to measure the output power generated from the transducer rather than the input power applied to the transducer [2]. The ultrasonic power entering the solution (in this case, distilled water) was estimated by an adiabatic measurement of the temperature rise just after the onset of ultrasonic irradiation (within 10 s). The following equation was used to estimate the power output of the ultrasonic transducers

$$P = \frac{mc(T_2 - T_1)}{t_2 - t_1} \quad (1)$$

where $P$ is the power output, $m$ the mass of the media, $c$ the specific heat of the media, $T_1$, $T_2$ the temperature, and $t_1$, $t_2$ the time.

The ultrasonic bath was surrounded by heat-insulating materials (Fig. 3) and the medium was constantly stirred with a pencil-stirrer throughout the adiabatic measurement. Temperature rise was recorded using a high-speed $X$–$Y$ recorder. The heat generated by

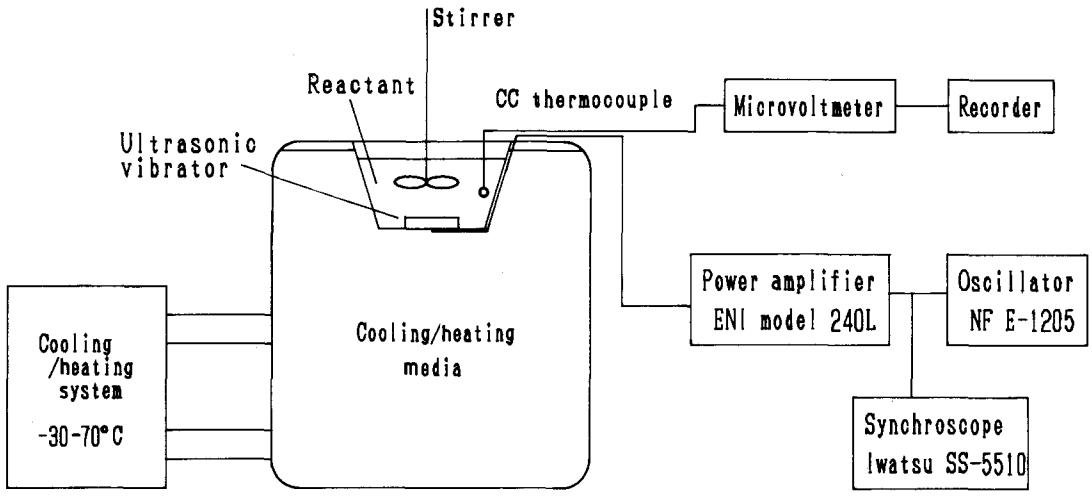


*Figure 2* Schematic diagram of the ultrasonic apparatus.

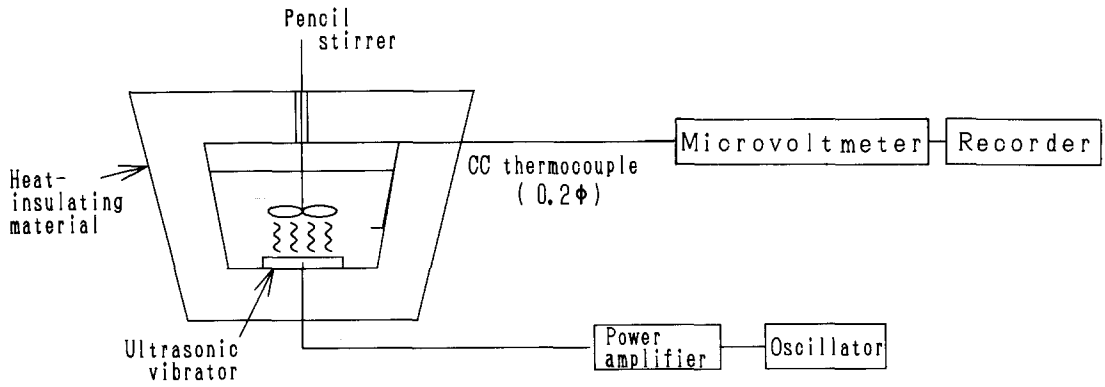


*Figure 3* The apparatus for adiabatic measurement of ultrasonic energy output.

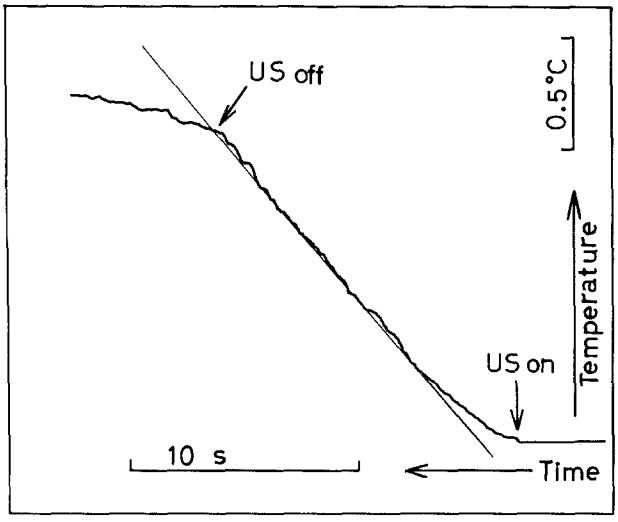


*Figure 4* Typical temperature rise curve for adiabatic measurement of ultrasonic power output. Frequency 1740 kHz.

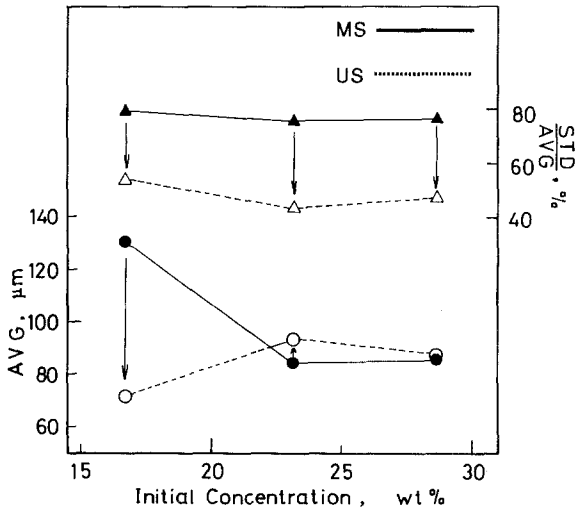


*Figure 5* The influence of initial concentration on the action of ultrasound: 550 kHz, 2.1 W cm$^{-2}$.

mechanical stirring was assumed to be negligible in these measurements. Fig. 4 shows typical results of such measurements.

Because ultrasonic energy is generally expressed in terms of intensity, defined as the average rate of flow of energy through a unit area normal to the direction of ultrasonic wave propagation as a result of sound pressure acting in that area, the power output obtained was further converted to acoustic intensity by using the equation

$$I = \frac{P}{A} \tag{2}$$

where $I$ is the acoustic intensity, $P$ the power output, and $A$ the cross-sectional area of the ultrasonic transducer. The intensities thus determined for the transducers used in this experiment were found to be 200 kHz 1.1 W cm$^{-2}$, 550 kHz 2.1 W cm$^{-2}$, and 1740 kHz 9.2 W cm$^{-2}$.

### 2.4. Evaluation

The Alum crystals precipitated from supersaturated solution were observed by optical microscopy. They were dipped into cedar oil for ease of observation. In order to evaluate the size distribution of the crystals, 1000–3000 particles for each sample were analysed using a Luzex-5000X image analyser (Nireco, Japan). Average particle size (AVG), as well as standard deviation (STD) of the particle size distribution, was obtained for each of the MS and US-treated samples.

## 3. Results

### 3.1. Effect of solute concentration

The relationship of average particle sizes of the precipitated Alum crystals with respect to initial solute concentration in the solution is shown in Fig. 5. Apparently, ultrasonic irradiation was very effective in refining the particle sizes and/or distribution compared to mechanical stirring. This is especially true for less-concentrated solution (i.e. 16.7 wt %) where the particle size was reduced from 130 μm of the MS-treated to 70 μm of the US-treated samples. For initially saturated or over-saturated solution (i.e. 23.1 or 28.6 wt %), both MS and US rendered essentially the same average particle sizes. However, the particle size distribution was greatly homogenized judging from Fig. 4, where the values of STD/AVG were all lower in the US samples than the MS samples.

### 3.2. Effect of ultrasonic frequency

The optical microscopy of the MS and US-treated samples (23.1 wt %) are illustrated in Fig. 6a–d. The particle size distribution of the MS sample was widely spread out as shown in Figs 6a and 7a, some are as large as ~ 2000 μm. Ultrasonic treatment greatly improved the uniformity of the precipitated particles, as can be seen in Figs 6b–d, or 7b. Also from Fig. 6, we see that the average particle size of the 200 kHz 1.1 W cm$^{-2}$ treated sample was the smallest, 550 kHz 2.1 W cm$^{-2}$ the next, and 1740 kHz 9.2 W cm$^{-2}$ the largest. The effects of ultrasonic treatment on the particle sizes and distribution are discussed based on nucleation and growth mechanism in Section 4.

### 3.3. Effect of acoustic intensity

The relationships of average particle size (AVG) and distribution (STD/AVG) with respect to acoustic intensity is depicted in Fig. 8. From this figure, it is seen that higher intensity ultrasonic treatment resulted in a larger average particle size after cooling from 60 °C to 30 °C in a 40 min time span. Also, particle sizes were more evenly and narrowly distributed (i.e. greater uniformity/homogeneity of particles) with ultrasonic treatment such that their STD/AVG values were lower than that of the MS sample.

## 4. Discussion

Nucleation occurs as a consequence of undercooling and collision [3], if stirring is applied, among the solute molecules. Particles precipitate from a supersaturated solution when a critical nucleation size is

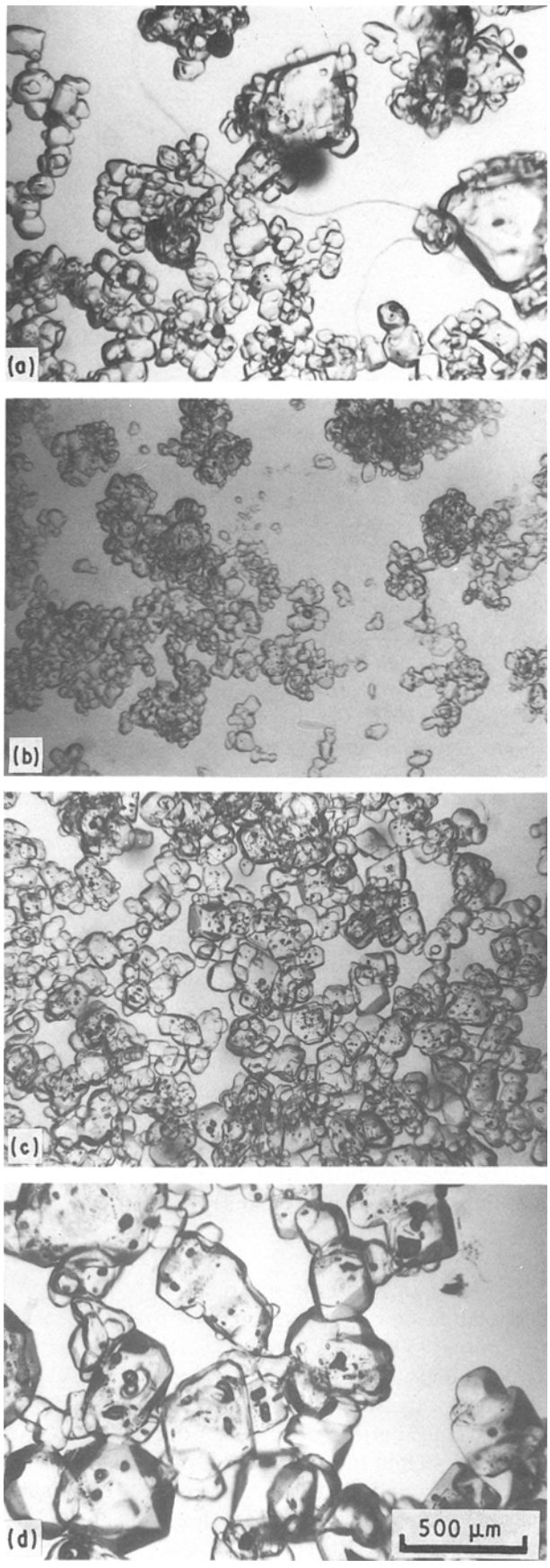


*Figure 6* Optical photomicrographs of (a) MS, (b) 200 kHz, (c) 550 kHz, (d) 1740 kHz treated samples of Alum.

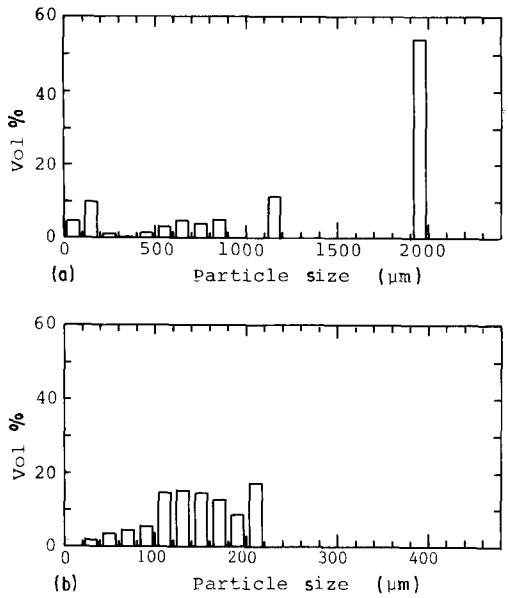


*Figure 7* Particle size distribution of (a) MS, (b) US (550 kHz) treated samples. (a) $AVG^3 = 5.3 \times 10^6$ μm$^3$, $STD^3 = 1.5 \times 10^8$ μm$^3$, (b) $AVG^3 = 7.0 \times 10^7$ μm$^3$, $STD^3 = 1.7 \times 10^8$ μm$^3$.

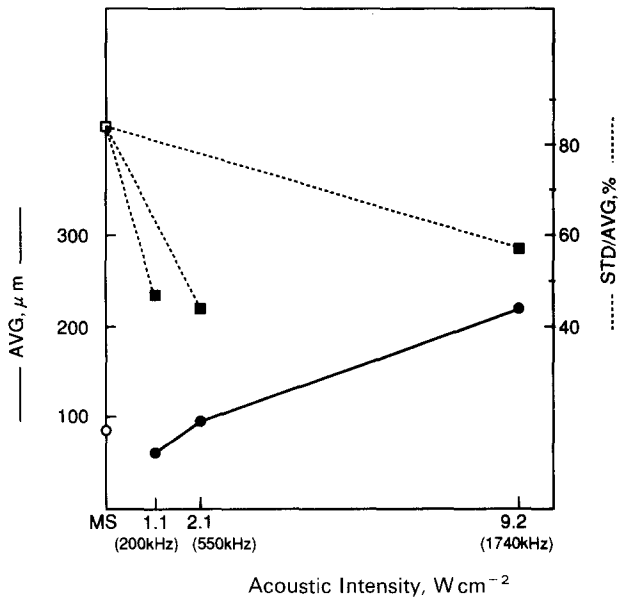


*Figure 8* The effect of acoustic intensity on average particle size and distribution. (—.—) 1740 kHz, (– – –) 550 kHz, (——) 200 kHz.

reached. Collision of molecules promoted by stirring will make the metastable region of recrystallization become smaller, as illustrated in Fig. 1. The probability of collision could, as the most simplified representation, be estimated by the kinetic energy of the particles. It is known that the motion of "clusters", particles smaller than the size of the critical nucleus, is not affected by macroscopic stirring because the kinetic energy of a single particle, $E_T$, decreases with decreasing particle size according to the equation [4]

$$E_T = C\varepsilon r^5 \quad (3)$$

where $r$ is the magnitude of a particle, $\varepsilon$ is the energy of stirring per unit volume and time. The constant $C$ is dependent on the density of particles and the viscosity of the fluid. However, the energy of sufficiently small particles is only dependent on Brownian motion [4].

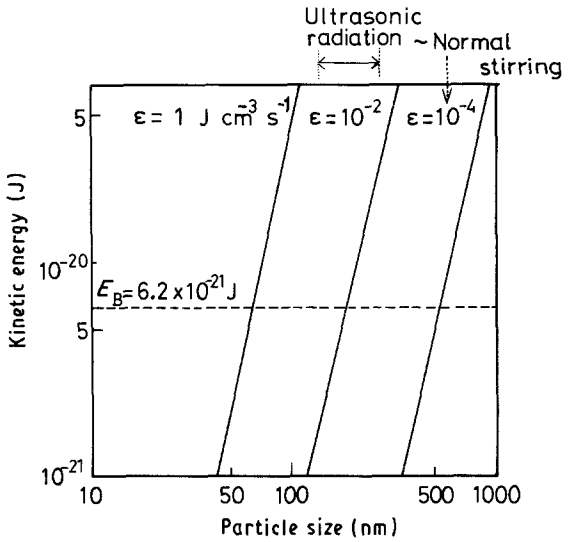


*Figure 9* Kinetic energy of a solid particle in a liquid as a function of its size. ε is the stirring energy.

The kinetic energy of Brownian motion $E_B$ is a linear function of temperature, $T$ [4]

$$E_B = 3kT/2 \quad (4)$$

where $k$ is the Boltzmann constant and $T$ the temperature. Fig. 9 compares these two kinetic energies of a particle as a function of size for several intensities of fluid agitation. In mechanical stirring, ε is about $10^{-4}$ J cm$^{-3}$ s$^{-1}$. In the ultrasonic case, it was estimated from the results of output power measurement to be about 0.5 J cm$^{-3}$ s$^{-1}$ for the strongest irradiation in this investigation. The energy of particles in mechanical stirring obviously was not sufficient for the necessary collision to occur such that the resulting particle sizes varied widely. The collision motion stemming from ultrasonic vibratory waves certainly contributes to the homogeneity in particle sizes of the precipitated Alum crystals. As far as the average particle size is concerned, however, the degree of undercooling on a microscopical scale, where the critical size of the nuclei formed may have played a more important role in determining the final particle size of the recrystallized Alum in this study.

Particles have to be nucleated before going into the growth phase. At approximately the same cooling period of 40 min for all treatments in this experiment, the final crystal sizes would be essentially controlled by the initial critical size of nucleation. The critical nucleus size, $r^*$, taking the equation for homogeneous solidification from the melt [5] and extending it for recrystallization from a liquid solution, is expressed as

$$r^* = \frac{2\gamma_{SL} T_m}{L_v} \frac{1}{\Delta T} \quad (5)$$

where $r^*$ is the critical nucleus, $\gamma_{SL}$ the solid/liquid interfacial free energy, $T_m$ the melting temperature, $L_v$ the latent heat of fusion per unit volume, and $\Delta T$ the undercooling. Assuming $\gamma_{SL}$, $T_m$, and $L_v$ are essentially the same at the time of nucleation, the critical nucleus size is inversely proportional to the degree of undercooling, $\Delta T$. Presumably, higher acoustic intensity would cause the local temperature to increase more than that of the low-intensity one. This would in terms result in the least degree of undercooling for the Alum solution irradiated with 1740 kHz 9.2 W cm$^{-2}$ intensity, such that the critical nucleus, $r^*$, is also the largest. This is exactly what is observed in Fig. 6b if comparing it with Fig. 6c or d. This phenomenon is also illustrated quantitatively in Fig. 8 where it shows that the average particle sizes of the higher acoustic intensity are larger.

## 5. Conclusions

1. Ultrasonic irradiation promotes the homogeneity in particle sizes of crystals precipitated from a supersaturated Alum solution.

2. Average particle sizes of both the MS and US-treated samples did not change much if the initial solute concentration was beyond the saturation solubility of the solution at elevated temperature.

3. Mechanical stirring may have promoted the nucleation of the Alum crystal from the supersaturated solution. However, its macroscopical stirring effect resulted in a widespread particle size distribution.

4. Higher acoustic intensity resulted in larger average particle size when the solution was slowly cooled for recrystallization. Thus, the average particle size was the largest for the solution irradiated with 1740 kHz 9.2 W cm$^2$, the second for 550 kHz 2.1 W cm$^{-2}$, and the smallest for 200 kHz 1.1 W cm$^{-2}$.

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